PESTICIDE RESIDUES IN SOILS

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Agricultural pesticides are now so widely used that few crops are grown without the use of one or more fumigants, fungicides, herbicides or insecticides applied to either plants or soil. Soil residues may come either from chemicals applied directly to control soil pests or diseases, or may reach the soil accidentally when plant foliage is sprayed to kill aerial insects or pathogens. Aerial spraying is often inefficient and it has been estimated that as much as 50% of sprays applied to foliage may ultimately reach the soil. Many of the chemicals that are applied are short-lived and create no residue problem; this is true of most fungicides and herbicides which seldom persist in the soil for longer than a single growing season.

Insecticides, particularly the chlorinated hydrocarbons, may persist much longer than this and require more discrimination in their use. Most of the subject matter of my talk will be concerned with insecticides, but other pesticides will be mentioned where appropriate and most of our discussion of the soil and environmental factors that affect the persistence of insecticides can be equally applied to other pesticides.

Although problems arising from persistent soil insecticide residues have been widely discussed, there have been few extensive random surveys designed to establish the levels of residues of various insecticides common in different types of cultivated soils. One of the better surveys made on 227 urban soils in Michigan in 1963/4 (Fahey et al.), showed very large residues of some chlorinated hydrocarbon insecticides ranging from a mean of 2.97 p.p.m.* for DDT and related materials, and 1.20 p.p.m. for chlordane to residues of only 0.04 p.p.m. for BHC, 0.03 p.p.m. for heptachlor and dieldrin, and no significant traces of aldrin. A survey of 32 arable soils in Ontario in 1964/5 (Harris et al.) showed a mean level of 1.2 p.p.m. of DDT and related materials in cereal-growing soils, 9.5 in vegetable-growing soils and 61.8 in orchard soils. The combined levels of heptachlor, chlordane, aldrin, dieldrin, endrin and endosulfan were only 0.4 p.p.m. in cereal soils and 1.6 p.p.m. in vegetable soils; none at all were found in orchard soils. In Illinois an intensive survey of 35 corn fields (Decker et al.) found no residues greater than 1.3 p.p.m. of aldrin and dieldrin even after annual

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* one p.p.m. approximates to 2 lb. active ingredient per acre.

treatment with up to 3 lb. active ingredient of these insecticides per acre for as long as ten years. Data from a survey of 21 potato-growing fields in England in 1962 (Wheatley et al.) reported no residues greater than 1.0 p.p.m. and again the larger residues were principally DDT. There have been numerous surveys of orchard soil in the United States which have estimated very large quantities of DDT, amounts of nearly 100 lb. a.i. per acre not being uncommon and the largest amount recorded being as much as 362 lb per acre.

Most insecticides break down exponentially but I have postulated that there may be several phases to the breakdown. Some of the insecticide may be lost during the application, followed by a phase of rapid loss when probably the insecticide is volatilizing. During the second phase the insecticide may still volatilize but some may also be leached or penetrate into the soil and become adsorbed on to various soil fractions. Finally, in the third phase more may be leached but most losses are by enzymatic breakdown probably by bacteria.

Calculations I have made from the extensive data on the rate of breakdown of soil insecticides available in the scientific literature (Edwards, 1966) show that on average DDT is the most persistent insecticide with an annual loss from soil of 25% of the amount present, dieldrin disappears at a rate of 28% annually, lindane 33%, chlordane 52%, heptachlor 54%, and aldrin 66%. Some of these losses however may represent transformation into other insecticidal chemicals e.g. aldrin becomes dieldrin, heptachlor becomes heptachlor epoxide and DDT breakdown products include other forms of DDT and DDE. By comparison, organophosphorus insecticides that are being used in soil, disappear rapidly, none remaining in appreciable amounts after a single growing season. Because they do not present serious residue problems there is less information on the rate of breakdown of organophosphorus insecticides. In my own work I have found that on average, 35% of the parathion present may disappear every month and about 30% of the diazinon in the same time. Chlorfenvinphos, Trithion (carbophenothion) and Zinophos are rather more persistent and dimethoate, disulfoton, phorate and Guthion (azinphosmethyl) rather less persistent. Of the fungicides, only quintozene may persist for a period of months and among the herbicides, MCPA, 2,4-D and dalapon may remain in soil for several weeks and 2,4,5-T, simazine, atrazine, propham and monuron which are listed in order of increasing persistence may remain in soil for periods up to year or even slightly longer. It is only when pesticides take longer than a year to breakdown and treatments are repeated annually, that accumulations are possible and only when annual treatments are large and the residues slow to dissipate that serious accumulations can be expected.

2. Factors affecting persistence of pesticides in soil

The most important single factor affecting the persistence of an insecticide in soil is its chemical structure and I hope this has been made clear from the preceding discussion. Probably the two most important properties of the insecticide affecting persistence are its volatility and solubility. DDT which is the most persistent insecticide is the least volatile and is also the least soluble organic chemical yet known. Dieldrin is also only slightly soluble and volatile whereas lindane and aldrin are much more soluble and volatile. Most chlorinated hydrocarbon insecticides are very insoluble which means that losses of residues from soil by leaching are not likely to be rare. By comparison organophosphorus insecticides are more soluble and leaching is much more likely.

The type of soil to which the insecticide is applied is the next most important factor and in a particular soil the organic matter content is the characteristic which has most influence. The organic content of soil may vary from 40 to 50% in muck soils down to less than 1% in some sandy soils and the surface of this organic matter provides a ready substrate on which pesticides may become adsorbed. The adsorption is not simple and although insecticides persist longer in soils with much organic matter, the effectiveness of the insecticide may not be any greater because the chemical is usually bound up in a non-toxic form. Other soil characteristics such as clay content, mineral content and soil structure also influence a sorption of the insecticide but their importance remains to be fully assessed.

The amount of rainfall is important in determining how long residues persist, reducing residues in several ways. Firstly the more soluble insecticides are readily leached into the drainage waters by heavy rain and even the more insoluble residues may be washed down into the soil as particles through cracks and crevices; in excessive rainfall the soil surface may become flooded and the insecticide carried away by surface run-off. Furthermore, the soil moisture may control the availability of the insecticide, because it has been demonstrated that in dry soils insecticides become bound to the mineral fraction of soil and unavailable to kill pests until the soil is rewetted. This is probably because the molecules of insecticide compete with water molecules for sites on the soil particles. Insecticides differ in the ease with which they become bound to dry soil in this way. For instance DDT and parathion appear to be much less strongly adsorbed on to dry soil than heptachlor and diazinon. Thus soils that are continually moist probably lose insecticide residues much more rapidly than those which are usually dry.

The soil temperature is probably less important in affecting the persistence of soil insecticides than soil moisture content because it varies less over the year, but it still exerts a very considerable influence on the rate of breakdown, and its action may be complex like that of soil moisture. Increased temperatures can greatly accelerate the rates at which volatilization, chemical degradation and bacterial decomposition occur; they may decrease the adsorption and release insecticide and increase the solubility of the insecticide. Higher temperatures may also make the soil very dry however, and this can in turn bind insecticides tighter to the soil and decrease their rate of disappearance. The overall affect however is probably for higher temperatures to accelerate the rate of insecticide losses.

The cultivation of the soil also affects the disappearance of residues; if the soil is not cultivated after the insecticides reach the surface, they may disappear as much as ten times faster than if they had been incorporated into the soil. Conversely frequent soil cultivation, by bringing residues to the soil surface where they may be weathered and volatilize more, may accelerate their disappearance.

It has been clearly shown that the microbial population of soil can exert a considerable influence on the persistence of insecticides; in autoclaved soil, insecticides may persist several times longer than in unsterilized soil. The proportion of soil insecticides that are broken down by microorganisms is still not established but it is an interesting speculation whether addition of suitable bacteria to soil could be a means of breaking down unwanted residues.

There are a number of minor factors that may also influence insecticide persistence in soil and under this heading we can consider the formulation and concentration of the insecticide. For instance water-soluble formulations leach more readily from soil than oil-soluble ones, and the particle-size greatly influences the rate at which the insecticide becomes adsorbed onto the soil particles. To summarize, insecticides usually persist longer in soils as granules than as emulsions, which in turn persists longer than miscible liquids. Wettable powders and dusts disappear fastest. There is good evidence to show that insecticide residues disappear proportionately faster from a small dose than from a large one. This does not mean, however, that larger gross amounts do not disappear from soil treated with large doses. It has also been shown that insecticide residues disappear more slowly from soil which is cropped, than from bare soil; this is probably due to the shading from the sun and wind, both of which may influence volatilization losses.

To summarize these points it seems likely that insecticides will disappear fastest from a well-cultivated, moist, warm soil which has little organic matter.

3. Effects of residues on plants.

Large residues of chemicals in soil can depress growth or germination, cause chlorosis or wilting, distortion and stunting or may be taken up into plants and produce off-flavors or taints in the edible part of the plant. Some may even stimulate growth. It is obvious that fumigants and herbicides will seriously injure plants growing in treated soil before all the residues have disappeared. Insecticides are not usually phytotoxic at the dosages normally applied to agricultural land and even large residues may be only slightly damaging. BHC which is the most phytotoxic of the chlorinated hydrocarbon insecticides readily produces taints or off-flavors in root crops growing in soil containing as little as 1/2 lb. of active ingredient per acre. Tomatoes, cucumbers, and beans are the most sensitive crops but at doses as high as 100 lb. per acre in the soil few crops will grow at all; such levels are very unlikely. By comparison DDT is only slightly toxic to a very few crops; again tomatoes, cucumbers and beans are the sensitive crops, and no other crops are affected at doses below 20 lb. a.i. per acre. DDT may stimulate the growth of carrots and other root vegetables. Aldrin and heptachlor are a little more phytotoxic than DDT, the same crops, together with beets and cereals being sensitive to these chemicals. Chlordane is more harmful than heptachlor but is still relatively safe, and dieldrin is the least phytotoxic of all the chlorinated hydrocarbons. Most of the organophosphorus insecticides are less phytotoxic than chlorinated hydrocarbons and many of them slightly stimulate growth.

4. Effects of residues on soil microorganisms.

Microorganisms are often sensitive to chemicals in soil and pesticides vary much in their effects on the soil microflora. Fumigants have the greatest effect killing most bacteria but being particularly lethal to the nitrifying bacteria, so that often ammonia accumulates in soil that has been fumigated; this increases available nitrogen and stimulates plants' growth. The effect of herbicides on soil organisms has been extensively investigated and normal rates of application appear to do little damage to the soil microflora; similarly insecticides do little harm to these organisms. BHC has the largest effect; aldrin, DDT, and organophosphorus insecticides such as parathion, have often stimulated microbial activity in soil.

5. Effects of residues on soil animals.

Enormous numbers of small invertebrate animals are present in soil, feeding on each other, on decaying matter or on plant roots; it is still not clear how important these animals are in turning over soil and maintaining its fertility. Burrowing animals, particularly earthworms greatly enhance mixing of soil and improve its aeration and drainage. It is interesting to speculate if their importance will increase if the newer agricultural techniques of minimal cultivation become widely adopted. Soil cultivation greatly decreases numbers of soil invertebrates, often nearly as much as pesticides, but it takes only a few months for populations to reestablish themselves.

The numbers of animals killed by soil insecticides may be closely correlated with the effectiveness of the chemical in killing soil pests, particularly if the insecticide is a broad-spectrum one. The more thoroughly the insecticide is mixed into the soil the more animals are killed. The proportion of invertebrates killed is usually related to the product of the toxicity of the pesticide and its persistence in soil; a very toxic chemical with a short life in soil may reduce populations as much as a less toxic but very persistent chemical. An example of the latter situation is when soil is treated with a fumigant. Most fumigants are very toxic to soil animals as well as microorganisms, killing as many as 98% of all the invertebrates in soil. When such a drastic effect occurs only a few species return at first and it can take as long as two years for the soil population to recover its original structure, although the chemical had completely disappeared in a few weeks.

One of the main effects of soil insecticides is to disturb the complex predator/prey relationships that commonly exist. A typical example lies in the use of DDT or BHC in soil, which invariably results in an increase in the number of small springtails. This is because the larger predatory mites which feed on these animals are more susceptible to the insecticide and the springtails are little affected by the chemical. Similar increases in numbers of springtails or small mites are common when organophosphorus insecticides are applied to soil, but these only rarely persist into a second growing season.

Aldrin and dieldrin are very toxic to beetles and fly larvae and some mites and springtails but do not appreciably reduce numbers of predatory mites or earthworms. DDT is rather less toxic to most animals than aldrin but is very lethal to the predatory mites. The groups of animals killed by lindane are similar to those susceptible to DDT, but BHC is a more effective soil insecticide than DDT, probably due to its greater volatility. Chlordane and heptachlor resemble aldrin in their spectrum of activity but differ in that they are very toxic to earthworms.

Most of the organophosphorus and carbamate insecticides applied to soil have now been tested for toxicity to soil invertebrates and in general they are much less toxic than the chlorinated hydrocarbons. Phorate is very toxic to earthworms, carbaryl (Sevin) somewhat less so and disulfoton and thionazin also reduce earthworm populations significantly.

Disturbance of predator/prey relationships has sometimes resulted in increased pest attacks although these are not common. In England the large predatory beetles that prey on the eggs of cabbage maggots are more susceptible to dieldrin than the eggs so that at a level of about 1 lb. a.i. of dieldrin per acre there is often a heavier attack of maggots than when no insecticide is used. Similarly in California, controlling a wireworm in lima bean fields with soil insecticides, caused an increased attack by seed corn maggot upon which the wireworm preys.

Excessive residues of insecticides remaining in soil are likely to increase the number of pests that are resistant to insecticides. This has happened with the cabbage maggot in England and Canada. Resistance usually builds up slower with soil pests than foliage pests because life cycles are usually longer, but with the continued use of large doses of persistent chemicals it is probable that many more instances of resistance will occur.

6. Better uses of soil pesticides.

Most of this talk has been concerned with the persistence of soil insecticides and their adverse effects. This is not to deny their value and it seems likely that soil insecticides will increase in use for many years to come. We might conclude this talk with a consideration of how insecticides may be used more sensibly and economically. Firstly, there is a need for an ideal soil insecticide which would be relatively specific for beetles and fly larvae, not be very toxic to mammals, have no harmful effects on crops microflora and microfauna, be slightly systemic and persist for about a single growing season; no chemical in current use has all these desirable qualities, but considerable efforts are being expended in testing new materials and it is hoped that better chemicals will soon be available.

It is impossible to thoroughly mix a very small quantity of an insecticide evenly through a large area of soil, so to be effective, soil insecticides must have some fumigant action or persist long enough for the longer-lived pests to pick up a lethal dose as they move through the soil.

It is now generally accepted that very persistent insecticides have drawbacks because although a single treatment may control pests for several years, there is no way of removing the residues from soil should they become undesirable. Many of the organophosphorus insecticides in common use are only effective for a few weeks and there is a real need for chemcials that will give protection for an entire season.

There are many ways in which we can improve the use of chemicals currently available. One of these is the better distribution and incorporation of broadcast insecticide treatments into the soil. To obtain maximum effect, the insecticide should be thoroughly mixed into the soil; merely plowing a surface spray or dust is insufficient. It is remarkably difficult to insure that an insecticide is spread evenly through the top six inches of soil; fortunately most of the soil pests are active in the upper three inches of soil where most of the insecticide lies even after thorough cultivation.

When broadcast treatments are applied, previous treatments of the land with persistent insecticides should be considered in relation to the known rates of breakdown of the insecticide to be applied. Relatively simple calculations enable such a dose to be used as will bring the already existing residues back to the level sufficient to control the pest. In this way excessive accumulations of persistent chemicals may be avoided with no loss of insecticidal efficiency and considerable economic gain.

Broadcast treatments may be necessary for some pests but there is an increasing tendency to place the insecticide as seed dressings or in bands close to the row or as spot treatments around each plant, wherever possible, such methods should be adopted, because they allow much more efficient use of the insecticide and smaller overall quantities of chemical may be used. Even persistent chemicals do not leave large residues in the soil when used in such a way. The dose applied should be related to the pest to be controlled; some insects may require large doses.

The formulation of the pesticide is of considerable importance in affecting its efficiency in controlling a particular pest. Insecticides which are inefficient in controlling some pests because they break down too rapidly, can have their persistence in soil extended by using the most suitable formulation. One way of achieving this is by coating the insecticides on to inert granules which hold it and gradually release it into the soil; in this way the life of an insecticide can be extended by as much as two or three times.

The adsorption of insecticides by soils containing much organic matter, in particular muck soils, has now become so well established that this factor should always be considered before deciding on the dose of an insecticide to be applied to soil. Usually a soil with abundant organic matter will require a great deal more insecticide to maintain the same efficiency in control of a pest; in such soils non-persistent chemicals are particularly desirable, so as to avoid accumulation of large residues of undesirable and inactive insecticide.

Finally, the phenomenon of the inactivation of insecticides in dry soils is becoming sufficiently well established to consider this in deciding the amounts of insecticides to be added to dry soils or to very moist ones. Much less insecticide may be equally effective in a soil that is predominately damp. The greater effectiveness of insecticides in moist soils may also be an added impetus to the use of irrigation where possible.

To conclude, there is little doubt that we shall need to use insecticides in soil to control pests for some considerable time yet, but as long as this is so we should endeavour to use less persistent chemicals where possible and if persistent chemicals are really necessary, they should be used in such a way that long term residue problems are unlikely to arise.

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